Process for preparing pigmented sol-gel compositions and these compositions

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Production of opaque pigment or filler-containing polysiloxane-based compositions by the sol-gel process involving first hydrolysing alkoxysilanes (obtained by reaction of silanes with metal alkoxides) to give a sol and then converting to a gel look that they are used as (1) in epoxy group-containing silane; and (2) pigments or fillers of average particle diameter> = 500nm.

Description of **DE10039404**

Coatings on the basis of organically modified Polysiloxanen are known. They have valuable physical and chemical qualities and stick very well on different subsoil (metals like steel, brass, aluminium, magnesium; ceramics; polymers; glass). They are mechanically resistant, e.g., against wear and chemically against the effect of almost all usually appearing chemicals. The known compositions are clear.

These coatings become about the so-called. Sol gel process made. Besides, hydrolysiert one Alkoxysilane and wins watery sole from mostly oligomeren, at times stable Organosilanolen capable of condensation which go over, in the end, in gels. The gels form if they have been raised on a substrate, in the end, by other dehydration or solvent denial suitable covers. A description of the Sol gel procedure which shows a sufficient introduction for the purposes of the present invention, for example, DE-A1-43 38 360 to whose contents is expelled instead of a repetition is to be taken. Different variations of the procedure or the compositions are also in the documents WHERE 95/13326 and WHERE 97/20005 described which form a background to the other explanation of the below described invention.

The Hydrolysat preserved Sol is able to modified, are provided i.e. with additions and is suited as coating means which would cross after the application on a substrate in a gel and, in the end, thermally to a bonded, ordinarily transparent (clear) cover can be condensed. Up to now for this reason Polysiloxangele were used, e.g., as covers for the improvement of the Kratzfestigkeit more optically of organic glasses.

The present applications have limited themselves, before all things because of the relatively high price of the raw materials, to a great extent to such coatings of sensitive surfaces, e.g., to lenses from organic polymers which should be made more scratch-resistant afterwards or usually resistant than this are over the polymers of themselves. In every case it was paid attention to the fact that the coatings remained, besides, more or less clear. As far as pigments were used (cf.

DE-A1-43 38 360), it always concerned extremely fine-piece, i.e. kolloide materials whose particle diameter was clearly small as the wavelength area of the visible light (400-800 nm), so that at most opaleszierende effects were received. Indeed, it is pointed out in that WHERE 95/13326 to the fact that itself with bigger particles (the document speaks of particle dimensions of several mu m) the hardness of the covers allows to increase, however, this tip is not followed up. This may also have been due to the fact that one has not succeeded up to now in training pigments or other fillers by a middle particle size more than 500 nm (0.5 mu m) in the restricted processing time enough homogeneous and in the required amount in the sole to be processed.

As already mentioned, the achieved layers in comparison to organic polymers show a relatively big hardness, nevertheless, are still relatively soft in comparison to inorganic materials. Hence, this stirs that it comes with the age-hardening, indeed, about the Silanolgruppen of the Siloxanoligomeren for a strong interlinking that, however, on account of her very low size (in molecular dimensions, i.e. <1 nm) the mechanical qualities, as for example hardness and wear permanence of the particles do not come for carrying. Indeed, by addition of small particles (size in the colloid area) from SiO2 (e.g., Aerosil Tm brands of the manufacturer DEGUSSA) the production of clear layers with raised wear firmness has succeeded. However, the added amounts in such particles are only low because the small particles own a high surface reactivity which leads to conurbation and with it viscosity rise.

Therefore a task of the present invention is the supply of an organically modified inorganic system which lies in his hardness clearly about in the state of the technology to described materials. In addition, the system also has to do the production more solidly, to the production of coatings of suitable interproducts with qualities steady for the time and the setting allow more variably of surfaces-physical and surfaces-chemical qualities, as for example Hydrophilie or Hydrophobie, also in combination with Oleophobie. Another purpose of the invention is more dyed the creation, with the Sol gel procedure of available compositions with valuable qualities as for example of high deck strength.

Up to now the covers which enter a certain lasting connection with the surface are used for the corrosion prevention by metal surfaces as a rule, e.g., by education of mixing oxide (with Pb3O4 on iron surfaces, with Cr2O3 on aluminium surfaces etc.) and according to the usual image reaction-sluggish sucked. Passivierungsschicht form. With these surface connections it is prevented that water can enter a reaction in connection with oxygen with the substrate material which leads to an at first superficial, later deep-passing oxidation of the metallic substrate. The quality has the Passivierungsschicht as a rule furthermore that it itself forms passivierte surfaces (basische Carbonate, Hydroxide, oxide) by dampness again. Pure organic varnish has the quality that they allow Permeation of steam and oxygen and offer with it no protection against the attack of dampness and oxygen for the metal surfaces. That's why one does not succeed in protecting metals like iron or aluminium without preceding Passivierung by the bare coating with organic polymer varnish against corrosion.

The organically modified inorganic coating materials preserved after the Sol gel procedure show, in principle, the same disadvantages like some surfaces-hard, purely organic covers, e.g., they are very friable and bend to the education of microtears (especially with change load bending stress). The surface can be damaged by this mike tear education and it can use corrosion.

The second task of the present invention is therefore the supply of an organically modified inorganic system which is suited, e.g., for the protection of metal surfaces without having at the same time the present disadvantages of suitable systems, as for example Sprödigkeit, mike tear education and bad liability on the substrate.

The protrudingly called tasks are solved by the procedure according to claim 1 or the compositions available with it (claim 9).

The production erfindungsgemässen Sols becomes at least one Organosilan of the general

formula (A1)
R <1> aR <2> bSiX (4a-b) (A1)
in R <1> for a not hydrolysierbaren rest, R <2> for one a functional group of weight-bearing not hydrolysierbaren rests and X for the same or different rests stands, are selected from hydrolysierbaren rests, the hydroxyl group and hydrolysierbaren substitution products of a hydroxyl group and an and b independently of each other ganzzahlige values of from 0 to 3 can accept and have an and b together the value 1, 2 or 3, or one of R <1> derived Oligomer, as well as if necessary
up to 70 Gew.-% of a Silans of the general formula (A2)
SiX4 (A2)
in X the preceding meaning has,
and/or at least of one hydrolysierbaren connection (A3)
to - if necessary modified, in the general one polycondensed at least partially oligomeren - Silanolen (A) hydrolysiert or.

Silicon connections A1

With erfindungsgemässen Organosilanen of the general formula (A1) it concerns the silicon connections which order more than two or mainly three hydrolysierbare rests and one or two, mainly a not hydrolysierbaren rest. In the approach of the chemistry of the macromolecular connections it concerns, just as with the below described connections A2 and A3 polymerisierbare monomers.

They show preferentially not hydrolysierbare rests (Substituenten) which carry for their part Epoxygruppen as functional groups. Therefore, the only one or at least one of both not hydrolysierbaren rests disposes of an Epoxidring.

Examples of hydrolysierbare rests X are a halogen (and the following, centilitre, Br and I, in particular centilitre and Br), Alkoxy (in particular C1-4-Alkoxy, as for example Methoxy, Ethoxy, n-Propoxy, i-Propoxy and Butoxy), Aryloxy (in particular C6-10-Aryloxy, e.g., Phenoxy), Acyloxy (in particular C1-4-Acyloxy, as for example Acetoxy and Propionyloxy) and Alkylcarbonyl (e.g., Acetyl). Especially preferential hydrolysierbare rests are Alkoxygruppen, in particular Methoxy and Ethoxy.

Examples of not hydrolysierbare rests R <1> for the purposes of the invention are Alkyl, in particular C1-4-Alkyl (as for example methyl, Ethyl, Propyl and Butyl), Alkenyl (in particular C2-4-Alkenyl, as for example vinyl, 1-Propenyl, 2-Propenyl and Butenyl), Alkinyl (in particular C2-4-Alkinyl, as for example Acetylenyl and Propargyl) and Aryl, in particular C6-10-Aryl, as for example Phenyl and Naphthyl) and the just called groups can show if necessary one or several Substituenten, as for example halogen and Alkoxy. Also Methacryl-and Methacryloxypropylreste earn in this connection mention.

Special examples of the functional groups of the rest R <2> are in particular the Epoxygruppe and further, e.g., at least one Hydroxy-, Ether-, Amino-, Monoalkylamino-, Dialkylamino-, Amido-, Carboxy-, Mercapto-, Thioether-, vinyl, Acryloxy-, Methacryloxy-, Cyano-, halogen, aldehyde, Alkylcarbonyl-, Sulfonsäure-or phosphorus acid group. These functional groups are bound about Alkylen-, Arylen-Alkenylen or bridge groups which can be interrupted by oxygen atoms or sulphur atoms or-NH-Gruppen to the silicon atom. The called bridge groups are derived, e.g., from abovementioned Alkyl-, Alkenyl-or Arylresten. The rests R <1> contain mainly from 1 to 18, in particular from 1 to 8 carbon atoms.

Prefers the epoxy-substituted rests R <2> contain in particular Glycidyl-or Glycidyloxygruppe. Examples of erfindungsgemäss applicable silicon connections A1 can be taken, e.g., to the pages 8 and 9 EP-A-195 493.

Erfindungsgemäss especially preferential silicon connections A are those to the general formula (I):
Of R3SiR' (I)
in the rests R, passed away or stand mainly identically, for a hydrolysierbare group (mainly C1-4-Alkoxy and in particular Methoxy and Ethoxy) and RE for Glycidyloxy-(C1-6)-Alkylen-Rest.

Because of his light availability it is used erfindungsgemäss in particular gamma-Glycidyloxypropyltrimethoxysilan (in the following shortened GPTS).

Silane A2

As in addition to silicon connection A1 applicable, completely hydrolysierbare connections (A2) of the general formula SiX4 those are suited whose hydrolysierbare rests are a halogen (and the following, centilitre, Br and I, in particular centilitre and Br), Alkoxy (in particular C1-4-Alkoxy, as for example Methoxy, Ethoxy, n-Propoxy, i-Propoxy and Butoxy), Aryloxy (in particular C6-10-Aryloxy, e.g., Phenoxy), Acyloxy (in particular C1-4-Acyloxy, as for example Acetoxy and Propionyloxy) and Alkylcarbonyl (e.g., Acetyl), Amino, Monoalkylamino, or Dialkylamino with mainly from 1 to 12, in particular to from 1 to 6 carbon atoms. Especially preferential hydrolysierbare rests are Alkoxygruppen, in particular Methoxy and Ethoxy.

Examples of the connections A1 and A2 which can be used are in the following to given and these should show, nevertheless, no restriction of the applicable connections.
Si (OCH3) 4, Si (OC2H5) 4, Si (O-n-C3H7) 4, Si (O-i-C3H7) 4, Si (OC4H9) 4, SiCl4, HSiCl3, Si (OOCCH3) 4, H3C-SiCl3, CH3-SI (OC2H5) 3, C2H5-SiCl3, C2H5-Si (OC2H5) 3, C3H7-Si (OCH3) 3, C6H5-Si (OC2H5) 3, (H3CO) 3-Si-C3H6-Cl, (H3C) 2SiCl2, (H3C) 2Si (OCH3) 2, (H3C) 2Si (OC2H5) 2, (H3C) 2Si (OH) 2, (C6H5) 2SiCl2, (C6H5) 2Si (OCH3), (C6H5) 2Si (OC2H5) 2, (i-C3H7) 3SiOH;
H2C=CH-Si (OOCCH3) 3, H2C=CH-SiCl3, H2C=CH-Si (OCH3) 3, H2C=CH-Si (OC2H5) 3, H2C=CH-Si (OC2H4OCl3) 3, H2C=CH-CH2-Si (OCH3) 3, H2C=CH-CH2-Si (OC2H5) 3, H2C=CH-CH2-Si (OOCCH3) 3, H2C=C (CH3)-COO-C3H7-Si (OCH3) 3, H2C=C (CH3)-COO-C3H7-Si (OC2H5) 3.

How evidently, the connections (A1) can also contain the not hydrolysierbare rests which show a C-C-Doppel-or triple connection. If such connections are used, others, olefinisch unsaturated, radikalisch polymerisierbare (mainly epoxy-or hydroxylgruppenhaltige) the monomers, as for example Meth (acrylate) can be added to the composition, in addition, also which can enter interlinkings with suitable conditions (cf. the following tips). Of course these monomers can also order more than two or more functional groups of the same type, as for example with Poly (meth) acrylaten from Polyolen; also the use of Polyepoxiden is possible. Then with the thermal or photochemically induced Härtung of the suitable composition a Polymerisation of the organic species takes place in addition to construction of the organically modified inorganic matrix by which the interlinking density and therefore also the hardness of the suitable covers and form bodies increases.

Other hydrolysierbare connections A3

In the end, counts to all above compositions that in addition to a silicon connection (A1 as well as if necessary A2) one or several other hydrolysierbare connections (A3) can be used which are derived from other central atoms than silicon and can build up an inorganic network.

As other hydrolysierbare connections (A3) are suited connections of the elements from the group

Zn, mg, Ti, Zr, Al, B, Sn and V which can become together with the connection (A1) and (A2) hydrolysiert so connections in general from alkaline earth metals and earth metals as well as the similarly behaving elements of the transitional metals. Nevertheless, the amount of such additional connections (A3) should not cross 70 Mol-% and in particular 50 Mol-% of all used hydrolysierbaren connections and especially does not prefer more than 30 and in particular no more than 10 Mol-% of all used hydrolysierbaren connections of that or the silicon connection (en) A1 or A1 and A2 have passed away.

Especially are preferred, e.g., Alkoholate by Ti, Zr or Al which have mainly the general formula (V)
M (OF OR' ") m (V)
in what M stands for Ti, Zr or Al, stands R' " for an Alkylgruppe with mainly from 1 to 4 carbon atoms (e.g., methyl, Ethyl, Propyl, Isopropyl or Butyl) and has n the value 4 (M = Ti, Zr) or 3 (M = Al).

A choice of being possible connections of the preceding group A3 is, e.g., the following:
Al (OCH3) 3, Al (OC2H5) 3, Al (O-n-C3H7) 3, Al (O-i-C3H7) 3, Al (OC4H9) 3, Al (O-i-C4H9) 3, Al (O-sek-C4H9) 3, AlCl3, AlCl (OH) 2, Al (OC2H4OC4H9) 3;
TiCl4, Ti (OC2H5) 4, Ti (OC3H7) 4, Ti (O-i-C3H7) 4, Ti (O-C4H9) 4, Ti (2-ethylhexoxy) 4;
ZrCl4, Zr (OC2H5) 4, Zr (OC3H7) 4, Zr (O-C4H9) 4, ZrOCl2, Zr (2-ethylhexoxy) 4 as well as Zr connections which show komplexierende rests, as for example beta-Diketon-and Methacryl leftovers;
BCl3, B (OCH3) 3, B (OC2H5) 3, SnCl4, Sn (OCH3) 4;
Sn (OC2H5) 4;
VOCl3, VO (OCH3) 3.

At least one silicon connection A1 or silicon connections A1 and A2 as well as if necessary at least one other hydrolysierbare connection A3 becomes or become common, mainly under use of a catalyst hydrolysiert. With this catalyst it should concern a sour catalyst, because basische catalysts are at the same time condensation catalysts what would entail that the Sol quality of the binding agents would get lost. A preferential sour catalyst is watery HCl. Besides, is so carried out the Hydrolyse mainly that per Mol to hydrolysierbarem rest about 1/2 Mol water uses, so a bigger profit in water is avoided.

Under the point of view of the macromolecular chemistry the resultant Silanole (A) are as precondensates to understand i.e. Oligomere which are as a watery sole and are stable at times and further condenses, can be polycondensed i.e. and be linked up, besides, as a rule. Then they are to be expected like, widely indissolubly. Nevertheless, this scientific approach should limit the invention in no way.

To these watery soles of Silanolen (A) are added erfindungsgemäss pigments or particle-shaped fillers in the farthest sense (" component of C ") which are bigger than the "nanoskaligen" particles used up to now. The erfindungsgemässen particles have a middle diameter which is bigger than which is possibly same from colloid particle, namely a middle particle size of 500 mu m or more, so or bigger than the middle wavelength of the visible light. As a middle particle diameter of pigments which are not isometrisch but in the form of small panels (as for example certain metal pigments), needles supra ä. are, the average value of the longest axis should count.

The particle-shaped fillers will be introduced especially advantageously in the form of premixtures (as a rule pastes-shaped or, nevertheless, viskosen Masterbatches) which assume a wetting of the particles with an organic mediator. Components of such premixtures are except the particles, above all, organic polymers, as for example acrylic polymers which possibly work as a mediator.

By the erfindungsgemässen installation of particle-shaped pigments other qualities can be "saddled" to the aimed gels. The layers show physical colours, are opaque in general (unless her index of refraction by chance or intentionally is identical with that of the Polysiloxan-basic body) and can be used in any creation. With it they have an appearance like conventional varnish

materials. Nevertheless, in contrast to these the resultant dry layer thickness is clearly degraded (approx. 10-15 mu m, towards 40-100 mu m with customary varnish, according to material).

In the end, it is suitable if weiterzukondensierenden Oligomeren (A) Glycidylreste show to take up to these one or several organic connections capable of condensation, not to press since aromatic and/or aliphatische Polyole (component B) with an average molecular weight from more than 1000 from which the image exists (which should not limit, however, the invention) that they can react with the Glycidylresten and cause therefore in addition to the interlinking about the Siloxanstruktur of the basic body a chemically different, additional interlinking.

Erfindungsgemäss to pigmented compositions stick much better than conventional materials on the surfaces. For example, can be renounced with an aluminium surface the Chromatierung usual up to now with chrome (VI) - connections. In the production of covers with sucked. To metallic varnish can be saved a majority by operations: Instead of more than 10 baths with the Chromatierung only 2-3 baths are required for an alkaline precleaning / Entfettung and activation of the surface:

<tb> <TABLE> Columns=2>
<tb> Head Col 1: Conventional varnish
<tb> Head Col 2: Erfindungsgemässe pigmented layers
<tb> 1. Chromatierung <SEP> alkaline precleaning
<tb> <TSB AL=L> 2-nd priming <SEP> Were cancelled
<tb> 3-rd metallic varnish <SEP> metallic varnish
<tb> 4-th varnish <SEP> Were cancelled
<tb> </TABLE>

Metallic varnish is applied in a layer and an operation and afterwards is branded. Even the brilliant degree of the coating can be put in one single layer exactly, without additional varnish layer.

By the installation of the aluminium pigmentation a raised corrosion prevention will receive. The flexibility of the coating after the age-hardening is improved compared with the unpigmented materials as with the Dorn-Biegeversuch can be shown.

Because of i. d. R. thinner layer and the raised solid state interest of the coating material the varnish consumption is decreased (environment) and the Lösemittelemissionen reduced.

To prepare the Organosiloxane (Organosilanole) for their part to the admission of the pigments, it is suitable and preferred erfindungsgemäss, intended to use Epoxidgruppen containing Organosilanole.

Hence, the invention further concerns a procedure to the production by compositions on the base by special hydrolysierbaren Silanen with Epoxidgruppen, the compositions available thereby and their use.

In particular the present invention concerns a procedure to the production by such compositions for coatings and form bodies with variable qualities.

Aromatic Polyole B

Erfindungsgemäss used aromatic Polyole (B) show an average molecular weight from at most 1000. Examples of such aromatic Polyole are, e.g., Polyphenylenether which carry in at least two of the Phenylringe Hydroxygruppen, as well as in general the connections in which two aromatic rings are connected by an easy connection, if necessary substituted, linear or branched Alkylen-

O-,-CO-,-SO2-etc. with each other and show at least (and mainly) a Hydroxygruppe in every aromatic group as well as Oligomere.

Therefore, especially preferential aromatic Polyole are aromatic Diole. Under this aromatic Diolen connections with the general formulae (II) and (III) are especially preferential:

EMI9.1
in what X for a (C1-C8)-Alkylen-or Alkyliden rest, a (C6-C14)-Arylenrest,-O-,-S-,-CO-or-SO2- stands and n immediately 0 or 1 is;

Preferential meanings for X in formula (II) are C1-C4-Alkylen or-Alkyliden, in particular-C (CH3) 2- and-SO2. In the connections of the formulae (II) and (III) the aromatic rings can carry beside the oh-groups still up to 4 or 3 other Substituenten, as for example halogen, Alkyl and Alkoxy.

Concrete examples of connections of the formula (II) and (III) are Bisphenol A, Bisphenol S. and 1.5-Dihydroxynaphthalin. Under this Bisphenol A erfindungsgemäss is especially preferred.

In the compositions for korrosionsinhibierende coatings the Polyol (Diol) is used as a rule in such amounts that per Mol Epoxidring from the silicon connection (A) from 0.2 to 1.5 Mol hydroxyl groups from the aromatic Polyol (B) are present. Mainly are per Mol Epoxidring from 0.3 to 1.2, especially from 0.6 to 1 Mol hydroxyl groups from the Polyol (B) prefers available and the optimum value lies with 0.8 Mol OH per Mol Epoxy. If aromatic Polyole with more than two oh-groups are used instead of aromatic Diolen, the suitable materials become more friable, for it, however, also harder.

Would be still to be mentioned that the index of refraction of the suitable korrosionsinhibierenden coatings can be steered not only by the concentration and kind of the particle-shaped materials (C) (if these are used) but also about the choice of the suitable aromatic Polyols. Thus, e.g., a coating under use of Bisphenol shows S. a higher index of refraction than one coating on the base of Bisphenol A. However, this fact plays with erfindungsgemäss with a pigment to full compositions only one subordinated role.

The qualities mentioned on top can be lent to the covers and form bodies from the suitable compositions by suitable choice and if necessary suitable combination of the above components (A) to (C), as well as other components (D, E . . cf. below) alternatively or cumulative.

In particular the combination of the particle-shaped material (C) with the hydrolysierten silicon connection (Silanol leads; A) to a composition for highly scratch-resistant coatings and form bodies. The erfindungsgemässen compositions can be also processed to thicker layers up to form bodies, without the area of the invention will leave.

In the end, the combination of vorhydrolysierter silicon connection (A) and aromatic Polyol (B) leads to a composition for korrosionsinhibierende coatings.

Of course several of the species (A, or A1, A2 and/or A3), if necessary (B) and (C) can exist in each case or are used.

In case of the composition for korrosionsinhibierende coatings the annexation of the particle-shaped material (C) leads to a higher Kratzfestigkeit of the suitable cover.

Further can be annexed to the compositions for highly scratch-resistant and korrosionsinhibierende coatings, in addition, to way known in itself a hydrolysierbare silicon connection with at least one not hydrolysierbaren rest which shows from 5 to 30 fluorine atoms to carbon atoms engagedly which are separated by at least two atoms of Si. The use of a such fluoridated Silans leads to the fact that to the suitable cover are lent, in addition, hydrophobe and oleophobe (dirty-unfriendly) qualities. A general description this fluorine-modified

Siloxanpolymeren is to be found in the already mentioned document WHERE 97/20005.

Especially in case of the compositions for hydrophile coatings and form bodies and korrosionsinhibierende coatings it is preferred furthermore to use, in addition, a Lewis base (D) or an Alkoholat (E) from Ti, Zr or Al as a catalyst for the Epoxid-Epoxid-or Polyol Epoxid interlinking.

Particle-shaped material C

Erfindungsgemäss is the middle particle diameter of the pigments resistant to temperature or particle-shaped fillers (C) at least 0.5, prefers from 0.5 to 10 mu m (500, or from 500 to 10,000 nm).

As pigments a wide scale of materials is suited.

Are called, for example:
White pigments: Titandioxid, zinc oxide, zinc sulphide and Lithopone
Black pigments: Soot (gas Russian, Furnace Russian, flaming Russian), Eisenoxidschwarz (Magnetit), Spinellschwarz
Blue pigments: Kupferphthalocyanine, Eisencyanblau (Miloriblau, Berlin blue), extremist marine blue, Spinellblau (Cobalt blue), Indanthronblau
Violet pigments: Dioxazinviolett
Green pigments: Chrome green and chrome real green, chrome oxide green, Spinellgrün (cobalt green), Phthalocyaningrün
Yellow pigments: Eisenoxidgelb, Bleichromat (Chrome-yellow), Wismutvanadat/-Molybdat, nickel and Chromtitangelb, yellow Azo-pigments, yellow Carbonylpigmente, yellow metal complex pigments
Red / orange pigments: Eisenoxidrot, Molybdatrot, red Azo pigments, red Carbonylpigmente, Chinacridone, Perylene, Diketo-pyrrolopyrrol pigments (DPP pigments)
Effect pigments: Iron gleam, golden bronze, pearl shine pigments, day luminous pigments
Metal pigments: Aluminium powder, zinc dust
Protective pigments against corrosion: Bleimennige, Chromate, phosphates

As fillers a wide scale of materials is suited. Are called, for example:
Earth alkali sulphates: Barium sulphate, calcium sulphate
Erdalkalicarbonate: Calciumcarbonat
Magnesium silicates: Talc
Aluminium silicates: Kaolin, gleam
Silicic acid: natural Guarzmehle
Fibers: Fiberglasses
Mike hollow balls: spherical Hohkörper of glass or another silicate material
Polyamide powder: Polyamide 11 or polyamide 12

Graphite

The pigments and fillers are preferred erfindungsgemäss in the form of pretreated, mainly pastes-shaped premixtures used which are partially available as commercial products and whose Herstellverfahren are known to a great extent. Untill customarily, they can be received, e.g., on below at the example of the aluminium pigments outlined way:
Aluminium pigments are produced by Vermahlung of round aluminium punches in ball mills in present from predominantly aliphatischen Lösemitteln and pastes-shaped concentrates are received. To the avoidance of "Kaltverschweissung" of the Al-Blättchen the Vermahlung occurs in present of "lubricants" (e.g., Stearinsäure, oil acid) which are absorbed in the metal surface and

prevent the Ausschwimmen of the pigments. Different types exist on Al pigments (Leafing-and NonLeafing types) and pigments with different surface treatment by thin-layered coatings (adjusting of the Hydrophilie/Hydrophobie). Such pastes can be covered by different manufacturers (e.g., corner kind works, Schlenck) as commercial products.

The pigment pastes which are acceptable with erfindungsgemäss used Polysiloxanen without phase dissolution are customary. So far are known, the suitable white pigments or coloured pigments or fillers become under high Scherung (ball mill, pearl mill, 3-roller etc.) under addition of certain acrylic resins dispergiert, until they are completely moistened. Such pastes can be covered by different manufacturers. The pigment interest varies according to pigment kind (Typical commercial products contained, for example: Titandioxid: 60%; flaming soot: 18%; Phthalocyaninblau: 12 or 20%; Eisenoxidrot: 58%). The Acrylatanteil lies between 25-45%. The rest exists of different Lösemitteln (2Methoxy-methyl ethyl acetate; Xylol, Ethylbenzol, Lösungsmittelnaphtha.)

Pearl shine pigment pastes contain non-metallic effect pigments from clear little sheets with high Brechzahl. It mostly concerns synthetic products from gleam on which one or several layers are raised by metal oxide. The pigment pastes exist of the pigment (15-60%) and an auxiliary binding agent in different concentration like Nitrocellulose (0-10%), Alkydharz (0-15%), acrylic resin (0-1%), Dibutylphthalat (0-60%), Lösemittel like Amylacetat (0-30%), Isopropanol (0-5%), Xylol, toluol, Butylacetat (0-35%). For example, the company The Mearl corporation, the USA offers commercial products.

Lewis base D

The transportation of the sole in gels happens preferentially by means of certain nitrogen connections which are used in particular in the compositions for hydrophile and korrosionsinhibierende materials ("Amin's hardener"; Lewis-bases). Such nitrogen connections can be selected, e.g., from N-Heterocyclen, amino groups to containing phenols, polycyclischen amine and ammonia (mainly as a watery solution). Examples are 1-Methylimidazol, 2-(N, N-Dimethylaminomethyl) phenol, 2,4.6-Tris (N, N-dimethylaminomethyl) phenol and 1.8-Diazabicyclo [5.4.0]-7-undecen. Especially preferentially 1-Methylimidazol are used. In addition, the presence of the Lewis base accelerates the interlinking of the gels about the Epoxygruppen capable of interlinking with Polyolen if these are used.

An other class of the nitrogen-containing Lewis bases (D) which can be used erfindungsgemäss are hydrolysierbare Silane which dispose of at least one not hydrolysierbaren rest which encloses at least one primary, secondary or tertiäre amino group. Such Silane can become together with the silicon connection A hydrolysiert and then show a Lewis base built-in on the organically modified inorganic network. Preferred nitrogen-containing silicon connections have the general formula (IV):
R3SiR " (IV)
in what the rests R are defined like for the connections (A1), and R " for one to Si to engaged, not hydrolysierbaren rest stands which encloses at least one primary, secondary or tertiäre amino group. Examples of silicon connections of the formula (IV) are 3-Aminopropyltrimethoxysilan, 3-Aminopropyltriethoxysilan, N-(2-Aminoethyl)-3-aminopropyltrimethoxyysilan, N-[N-(2-Aminoethyl)-2-aminoethyl] 3-aminopropyltrimethoxysilan and N-[3-(Triethoxysilyl) propyl)]-4,5-dihydroimidazol.

The Lewis base is used if the silicon connection (A1) shows Epoxygruppen in the suitable compositions in general in an amount from 0.01 to 0.5 Mol per Mol Epoxygruppe of the silicon connection (A1). Amounts in the area are preferred by from 0.02 to 0.3 and in particular from 0.05 to 0.1 Mol Lewis base per Mol Epoxygruppe.

For the other modification of the erfindungsgemässen compositions fluorine-containing silicon

connections (E) can be used. Such compositions prove not only highly scratch-resistant and korrosionsinhibierende coatings, but, in addition, work hydrophob and at the same time oleophob. These Silane (E) dispose of at least one not hydrolysierbaren rest which shows from 5 to 30 fluorine atoms to carbon atoms engagedly which are separated by at least two atoms of Si. Such Silane are described in the DE Os 41 18 184 in detail. Examples are the following:
C2F5CH2-CH2-SiY3
n-C6F13CH2CH2SiY3
n-C8F17CH2CH2SiY3
n-C10F22CH2CH2SiY3
(Y = OCH3, OC2H5 or centilitre)
i-C3F7O-(CH2) 3-SiCl2 (CH3)
n-C6F13CH2CH2SiCl2 (CH3)
n-C6F13CH2CH2SiCl (CH3) 2

These fluoridated Silane become in general in an amount from 0.1 to 15, mainly from 0.2 to 10 and especially prefers from 0.5 to 5 Gew.-%, covered to the solid salary of the organically modified inorganic matrix, used.

One mentions that the use of the silicon connections (A) which order more than at least two Epoxidgruppen leads in the erfindungsgemässen compositions to coatings and form bodies with improved robustness by condensation. The production of the erfindungsgemässen composition occurs in this area usual way. Mainly the hydrolysierbare silicon connection (A) becomes at first mainly under use of a sour catalyst and with ambient temperature hydrolysiert and, as mentioned, mainly about 1/2 Mol H2O per Mol hydrolysierbare group is used. The addition of the other components joins this then in any order. The particle-shaped material (C) can already attend during the Hydrolyse.

If more reactive connections (A3) are also used beside the relatively reaction-sluggish silicon connections, as for example such of Ti, Zr and Al, is recommended it to add the water gradually and/or under ice cooling and/or to use connections which had been limited in her responsiveness. an example of such connections is an Al (OCH2CH2OC4H9) 3).

To the setting of the rheologischen qualities of the compositions solvents on any step of the production can be added to these when required (mainly it concerns with these solvents alcohols liquid with ambient temperature which originate, for the rest, also with the Hydrolyse of the preferentially used alc. oxide of the concerning elements) and these alcohols can contain, in addition, Ethergruppen.

To further being able to erfindungsgemässen compositions the usual additives are added, like (dissolvable) colorings, course aids, Tenside, stabilizers against the influence of short-wavy light, photo initiators, Photosensibilisatoren (if a photo-chemical Härtung of the composition is intended) and thermal Polymerisationskatalysatoren. The compositions with which coatings should be produced can be raised on the substrate with standard procedure like diving, to pranks, brushes, Rakeln, rollers, spraying and catapults.

The usually connecting Härtung of the gels can happen gegegenenfalls after previous Abtrocknung with ambient temperature (to the partial distance of the solvent) as usual. Mainly this happens thermally at temperatures in the area of from 50 to 300 C DEG, in particular from 70 to 200 C DEG and especially prefers from 90 to 130 C DEG, if necessary under decreased pressure. If unsaturated connections and photo initiators had been coused, a Härtung can also occur through the radiotherapy which if necessary a thermal Nachhärtung joins.

The erfindungsgemässen compositions are suited in particular to the coating and the layer-thick amount, e.g., to from 1 to 30, in particular from 3 to 15 mu m. It gets on that the least layer thickness must be tuned to the particle size of the component (C).

The following examples should explain the invention further without limiting, nevertheless, their circumference. They use uniformly a Sol existing of two components gel-basic system with an aromatic Polyol and a hardener (amine component) which is especially preferred erfindungsgemäss. The Sol gel-basic system is improved one by Hydrolyse from gamma-Glycidyloxypropyltrimethoxysilan (GPTS) with 0.1 molarer HCl, Bisphenol-A as a Polyol, perhaps to a Lösemittel and an addition, that the course (here: polyethermodifiziertes silicone; product: e.g., Byk TM 306) preserved composition.

Family component

535,0 g s gamma-Glycidyloxypropyltrimethoxysilan (GPTS) are presented in the beginning vessel and are moved under stirring with 61.5 gs HCl (0.1 molar). With the exothermen reaction the beginning warms itself up within less minutes and becomes einphasig. After 10 minutes 203.5 gs Bisphenol-A are slowly added and solved under other stirring. The family component is clear to water and easily viskos.

Hardener component

In 188,8 gs Butylglykol 6.3 gs 1-Methylimidazol as well as for the improvement are solved by course and surface hardness 4.9 gs of a polyethermodifizierten silicone which is available, for example, under the trade name Byk 306.

Processing

Family component and hardener component become the production of a clear coating material in the mass relation 4: 1 zusammengegeben and by stirring homogenises. To the adjusting of the processing viscosity (e.g., for hose application) can be diluted with a polar Lösemittel (e.g., ethyl acetate, Butylacetat). After the application the age-hardening of the coating material occurs through branding: 15 minutes with 180 C DEG (in the flow stove), 45 minutes with 130 C DEG or 60 minutes with 100 C DEG. His full loading capacity reaches the hardened coating after 2 days of Nachhärtung with ambient temperature.

Example 1

Sol gel-basic system; aluminium pigment

16 gs of family component are diluted with 5 gs Butylacetat. In addition 1.5 gs of an aid which improves the Dispergierung are given. A 38%th solution of highly molecular Block-Copolymerer with pigmentaffinen groups which is under the name Disperbyk 163 in trade or a 50%th solution of a salt of unsaturated Polyaminamide and more down molecularly sour polyester, commercial product Anti Terra U) is suited, e.g. The pigmentation occurs through addition of 4.5 gs of a customary aluminium paste (examples of commercial products are possibly: Stapa Hydrolux 400; Stapa Metallux 2196; Metalure L 55700). The paste is distributed by stirring with low Scherung in the beginning. Before the processing are added to the pigmented family component 4 gs of hardener component, are homogenised by stirring. Processing / application and age-hardening as protrudingly described.

For the better adjustment of the aluminium particles in the coating (arrangement of the small slice-shaped metal spangles in parallel with surface) can be added to the described beginning 16 gs 20%th Cellulose-Acetobutyrat (CAB) solution. Moreover 100 gs Cellulose-Acetobutyrat are slowly added under stirring to a mixture of 175 gs Butylacetat and 225 gs Xylol, until the CAB is totally solved.

Example 2

Sol gel-basic system; pearl shine pigment with pigment paste (Silver-metallic effect)

160 gs of family component are diluted with 50 gs Butylacetat. In addition 15 gs of the protrudingly mentioned Disperbyk 163 or Anti Terra U are given. It is pigmented by addition of 10 gs of pigment paste (possibly Mearlin Nu-antique Silver 9110FROM, manufacturer The Mearl corporation). The paste is distributed by stirring at hohher speed and low mole forces. In addition are given for the processing 40 gs of hardener component and are homogenised under stirring. The setting of the hose viscosity occurs through addition of Butylacetat, processing / application and age-hardening like in example 1

Example 3

Sol gel-basic system; different coloured pigments (e.g.: Blazing red; RAL 3000)

10.8 gs Dispergieradditiv (50%th solution of an Alkylammoniumsalzes of a polycarboxylic acid, Bsp become 160 gs of family component: Anti-Terra TM-203) given. Under stirring FGR 70, 0.51 gs Bayferrox TM - Yellow 3910, 0.19 gs Bayferrox red 130 m, 0.32 gs Titandioxid R 211 and 13.1 gs of talc 20 M 2 become moreover 1.86 gs Constantly given. The beginning becomes 10 minutes with high mole strength dispergiert and then in a pearl mill up to a grain delicacy of 5 mu m vermahlen. Moreover 50 gs Butylacetat are given. In addition are given for the processing 40 gs of hardener component and are homogenised under stirring. The setting of the hose viscosity occurs through addition of Butylacetat. Processing / application and age-hardening like in example 1.

Example 4

Sol gel basic system; aluminium pigments, in addition, coloured pigmentation (Bsp: Blazing red; RAL 3000-metallic)

10.8 gs Dispergieradditiv (50%th solution of an Alkylammoniumsalzes of a polycarboxylic acid, Bsp become 200 gs of family component: Anti Terra 203) given. Under stirring FGR 70, 0.51 gs are given moreover 1.86 gs Constantly Bayferrox yellow 3910, 0.19 gs Bayferrox red 130 m, 0.32 gs Titandioxid R 211 and 13.1 gs of talc of the kind 20 M 2. The beginning becomes 10 minutes with high mole strength dispergiert and then in the pearl mill up to a grain delicacy of 5 mu m ground. Moreover become 62.5 gs Butylacetat and 6.25 gs of aluminium paste (example: Stapa

Hydrolux 400; Stapa Metallux 2196; Metalure L 55700) given. The paste is distributed by stirring after the recommendation of the manufacturer (avoidance of allzuhoher mole forces) in the beginning

In addition are given for the processing 50 gs of hardener component and are homogenised under stirring. The suitable hose viscosity is put by addition of Butylacetat. Processing / application and age-hardening like in example 1.

To the better alignment of the aluminium pigments in the coating material can be added to the described beginning 200 gs of 20%th CAB solution.

Example 5

Sol gel basic system; coloured pigmentation (tone: Light blue)

160 gs of family component are diluted with 50 gs Butylacetat. 15 gs Dispergieradditiv (38%th solution of highly molecular Block-Copolymerer with pigmentaffinen groups become this; example: Disperbyk 163 or 50%th solutions of a salt of unsaturated Polyaminamide and more down molecularly sour polyester (example: Anti Terra U) given. Pigmentation by addition of 8 gs of blue pigment paste (example: Lanco-Beit UN 565) and 8 gs of white pigment paste (example: Lanco-Beit UN 161). The paste is distributed by stirring with low mole strength. For the processing 40 gs of hardener component are added and homogenised under stirring. The suitable hose viscosity is put by addition of Butylacetat. Processing / application and age-hardening like in the prehired Herstellbeispiel described.

Example 6

Sol gel basic system; aluminium pigment + coloured pigmentation (blue-metallic)

160 gs of family component are diluted with 50 gs Butylacetat. 15 gs Dispergieradditiv (38%th solution of highly molecular Block-Copolymerer with pigmentaffinen groups become this; example: Disperbyk 163 or 50%th solutions of a salt of unsaturated Polyaminamide and more down molecularly sour polyester (example: Anti Terra U) given. It is pigmented by addition of 6 gs of blue pigment paste (example: Lanco-Beit UN 565), 6 gs of white pigment paste (example: Lanco-Beit UN 161) and 6.25 gs of aluminium paste (example: Stapa Hydrolux 400; Stapa Metallux 2196; Metalure L 55700). The pastes are distributed by stirring with low mole strength in the beginning

For the processing 40 gs of hardener component are added and distributed under stirring homogeneous. The suitable hose viscosity is put by addition of Butylacetat. Processing / application and age-hardening like in example 1.

For the better adjustment of the aluminium particles in parallel with surface of the coating can be added to the described beginning 16 gs of 20%th CAB solution.

Example 7

Sol gel basic system with a Periglanz pigment with a customary pigment paste to the achievement of a silvery-metallically gänzenden cover

160 gs of the family component of the Herstellbeispiels 1 are diluted with 50 gs Butylacetat. In addition 15 gs Dispergieradditiv (38%th solution of highly molecular Block-Copolymerer with pigmentaffinen groups (example Disperbyk 163 or 50 %ige solutions of a salt of unsaturated Polyaminamide and more down molecularly sour polyester, example Anti Terra U) are given. The pigmentation occurs through addition of 10 gs of pigment paste (example: Mearlin Nu-antique Silver 91 IOAB, The Mearl corporation) to the beginning. The paste is distributed by stirring at high speed and low mole forces in the beginning. In addition are given for the processing 40 gs of hardener component and are homogenised under stirring. The suitable hose viscosity is put by addition of Butylacetat. Processing / application and age-hardening like in example 1.

Claims of **DE10039404**

1. Procedures to the production of mainly opaque, pigments or fillers to containing compositions, in particular coatings, on the basis of Polysiloxanen by means of the Sol gel process and one in the first step by moving of Silanen with metal-alc. oxide available Organosilane (Alkoxysilane) would cross to a Sol hydrolysiert and the occasional stable watery Sol capable of condensation from mostly oligomeren Organosilanolen in the second step in a gel, use thereby marked, that one Epoxygruppen containing Silane and pigments or fillers of a middle particle diameter of at least 500 nm.

2. Procedure hardens to the production of compositions on the basis of hydrolysierbaren Silanen with Epoxidgruppen after claim 1, thereby marked that one does not give the engaged rest which disposes of an Epoxygruppe, at least one filler B, well-chosen from inorganic or organic pigments or fillers by an average particle size of at least 500 nm and an aromatic Polyol with an average Molgewicht from at most 1000 to at least one hydrolysierbaren or already vorhydrolysierten silicon connection (A) with at least to one hydrolytisch to splittable off, directly in silicon if necessary hydrolysiert and under dehydration.

3. Procedures after claim 1, thereby marked, that one to the production of the Sols

a) at least one Organosilan of the general formula (A1)
R <1> aR <2> bSiX (4a-b) (A1)
in R <1> for a not hydrolysierbaren rest, R <2> for one a functional group of weight-bearing, not hydrolysierbaren rests and X for the same or different rests stands, are selected from the hydroxyl group and hydrolysierbaren substitution products of a hydroxyl group and an and b independently of each other ganzzahlige values of from 0 to 3 can accept and have an and b together the value 1, 2 or 3, or an Oligomer derived of it,
b) if necessary a Silan of the general formula (A2)
SiX4 (A2)
in X the preceding meaning has, as well as
c) if necessary one or several other hydrolysierbare connections (A3) whose central atoms of silicon have passed away, in particular from the group Ti, Zr, Al, B, Sn and V which can earth together with the connection (A1) hydrolysiert and build up an inorganic network,
to - if necessary modified - Silanol (A) hydrolysiert.

4. Procedures after the claim 2, thereby marked that an Organosilan of the general formula (A1) is used in which at least one of both not hydrolysierbaren rests R1 is ordered of an Epoxidring and is added before or after which Hydrolyse of the Organosilans an aromatic Polyol.

5. Procedures after claim 4, thereby marked that as an aromatic Polyol a Polyol with an average molecular weight from up to 1000 is used, well-chosen from the group of the Polyphenylenether which carry in at least two Phenylenresten Hydroxygruppen, are connected as well as the connections, in which two aromatic rings by an easy connection, if necessary substituted, linear or branched Alkylen,-O-,-CO-or-SO2-with each other and show at least one Hydroxygruppe in every aromatic group.

6. Procedures after claim 5, thereby marked that as an aromatic Polyol a Polyol with one of the general formulae (II) or (III) is used

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in what X for a C1-8-Alkylen-or Alkyliden rest, a C6-14-Arylenrest,-O-,-S-,-CO-or-SO2-stands and n immediately 0 or 1 is;

7. Procedures after claim 5, thereby marked that as an aromatic Polyol Bisphenol A, Bisphenol S. and/or 1.5-Dihydroxynaphthalin are used.

8. Procedures after claim 2, thereby marked that as an other hydrolysierbare connection a connection is used by tin, magnesium, zinc, aluminium, titanium and/or zircon.

9. Composition, namely interproduct or end product, as it will receive one of the claims from 1 to 8 after the procedure.